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(54) Method of mass analyzing a sample by use of a quistor and a quistor designed for performing this method.

(57) A method of mass analyzing a sample comprises the steps of defining a three-dimensional electrical quadrupole storage field including an RF component and creating sample ions therein so that ions within the mass range of interest are simultaneously trapped and perform ion-mass specific secular movements. In order to analyse the trapped ions, an exciting RF field is generated, the frequency of said exciting RF field being equal to the frequency of secular oscillations of ions having a specific mass. By varying either the frequency of the exciting RF field or the frequency of the secular oscillation of the ions by modifying the quadrupole storage field, the resonance condition for the secular motion is varied in such a way that ions of consecutive masses encounter a resonance of their secular movements with the exciting RF field, so that they take up energy, increase thereby their secular movement, and finally leave the trapping field for being detected. The method is advantageously performed in a QUISTOR having field faults which result in non-harmonic oscillations of trapped ions.

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METHOD OF MASS ANALYZING A SAMPLE BY USE OF A QUISTOR AND A QUISTOR DESIGNED FOR PERFORMING THIS METHOD

The present invention is directed to a method of mass analyzing a sample according to the preamble of claim 1 and to a QUISTOR designed for performing this method according to the preamble of claim 10.

This method and a QUISTOR suitable for performing this method are described in US-A-4,540,884. The basic construction of the device called "QUISTOR" ("QUadrupole Ion STORe") or "Ion Trap" is described in US-A-2,939,952. In such QUISTOR, a radio-frequency hyperbolic three-dimensional quadrupole field is generated in which ions of different mass-to-charge ratios can simultaneously be stored. For a detailed introduction into the quadrupole technique including QUISTORs, see Peter H. Dawson (editor), Quadrupole Mass Spectrometry and its Applications, Elsevier, 1976.

The QUISTOR consists of a toroidal ring electrode and two end cap electrodes. A high RF voltage of amplitude V_{stor} and frequency f_{stor} is applied between the ring electrode and the two end cap electrodes. Both end cap electrodes are normally connected to the same potential. The radio-frequency voltage across the electrodes forms, at least near the center of the QUISTOR, a hyperbolic three-dimensional quadrupole field which is able to trap ions.

As shown in Fig. 1 which illustrates, schematically the design of the ring and end cap electrodes 1 and 2, respectively, cylindrical coordinates are used to describe its configuration. The directions from the center 3 towards the saddle line of the ring electrode 1 are called the r directions and the plane defined by said r directions is called the r plane. The z direction is defined to be normal to the r plane.

The ion oscillations by the RF field cause, integrated over time, a resulting force which is directed towards the center 3, and proportional to the distance from the center. This quasi-elastic central force forms, integrated over time, a harmonic oscillator for the ions. The relatively slower harmonic oscillations around the center 3 are superimposed by the faster impregnated RF oscillations.

The harmonic oscillations are called the "secular" oscillations of the ions within the QUISTOR field.

The exact mathematical description of the movements of ions in a QUISTOR is difficult. Up to now, a solution of the resulting partial equations was only possible for the special case of independent secular movements in the r and z directions. The solution of the corresponding "Mathieu"'s differential equations results in an "ideal QUISTOR" of fixed design: The slope of the asymptotic cone envelope has the "ideal angle" z/r = 1/1.414 (1.414 = square root of 2).

Most of the QUISTORs which have been built up to now, follow the design principles of such an "ideal" QUISTOR with hyperbolic surfaces and the above "ideal" angle z/r, although it has been shown experimentally that QUISTORs of quite different design, e.g. with cylindrical surfaces, do store ions by no means less effective.

In the special case of an "ideal QUISTOR", the secular oscillations are, by the inherent mathematical assumptions, independent and different in r and z directions. The stability area boundaries for the ion movements in the well-known a/q diagram shown in Fig. 2 can be calculated.The stability area is formed by a net of β_r lines ($0 < \beta_r < 1$) and crossing β_z lines ($0 < \beta_z < 1$). The β-lines describe exactly the secular frequencies:

$f_{sec,r} = \beta_r * f_{stor} / 2;$

$f_{sec,z} = \beta_z * f_{stor} / 2.$

In Fig. 2, the stability area for an "ideal" QUISTOR is shown in the a_z/q_z diagram, together with the iso-β lines.

For an ion having a given mass-to-charge-ratio m which is stored inside the stability boundaries given by the operating conditions a and q, there exists a unique secular frequency $f_{sec,z,m}$ (a,q) in the z direction and a (usually different) unique secular frequency $f_{sec,r,m}$ (a,q) in the r direction.

"Non-ideal" QUISTORs which are not built according to the above mentioned ideal design criteria, or which show a lack of precision in production, do not have independent r and z secular motions but secular oscillations in one direction which are coupled with the secular oscillations in the other direction. The secular movements influence each other mutually, and, as it is known from coupled oscillators, resonance phenomena appear. Depending on the type of field distortions, several types of natural resonances, like "sum resonances" or "coupling resonances ", exist in a QUISTOR.

Up to now, these resonances have been investigated and described only for the cases of superimposed weak multipole fields, see F. v. Busch and W. Paul, Z. Phys. 164 (1961) ,588. If the quadrupole field is superimposed by a weak multipole field, with one pole fixed in z direction, the conditions for sum resonances are:

Type of field:	most prominent resonance condition	Order of potential terms
quadrupole field:	none	second order, no mixed terms
hexapole field:	$\beta_z + \beta_r/2 = 1$	third order with mixed terms
octopole field:	$\beta_z + \beta_r = 1$	fourth order, with mixed terms and with equal signs for r^4, z^4 terms
dodecapole field:	$\beta_z/2 + \beta_r = 1$	sixth order with mixed terms

Each electrical field is a first derivation (with respect to r and z) of the electrical potential. The mathematical expression for the electrical quadrupole potential contains only quadratic terms in r and z, and no mixed term. In the case of multipoles, however, terms of higher order and mixed terms appear in the mathematical expression of the electrical potential. The mixed terms represent the mutual influence of the secular movements, and the terms of an order higher than 2 represent non-harmonic additions which make the secular frequencies dependent on the amplitude of the secular oscillations. (For the exact formulae of multipole potentials, see the cited book by Dawson).

The trapping field in the center of the QUISTOR is naturally mostly influenced by the shape of those parts of the electrodes which are nearest to the center. Thus, the curvature across the saddle line of the ring electrode and the curvature at the summit of the end cap electrodes influence the trapping field most. These curvatures can be described by inscribed circles 4 and 5, the one having the radius R_r for the ring electrode 1, and the other having the radius R_e for the end cap electrodes 2. In fact, a QUISTOR can be built by an O-ring shaped ring electrode and two spheres as end cap electrodes, just equivalent to a quadrupole mass filter which can be successfully built from four cylindrical rods, (Fig. 1). Then, the ideal QUISTOR is characterized by the following condition for the distance-corrected ratio Q of the described radii:

$$Q = \frac{R_e}{R_r} * \frac{r_0}{z_0} = 4.000 \quad \text{, wherein}$$

r_0 = smallest distance of the ring electrode 1 from the field center 3 and
z_0 = smallest distance of the end cap electrodes 2 from the field center 3.

If a non-ideal QUISTOR has end cap and ring electrodes which are both too "sharp" (the radii R_r and R_e are both too small), or both too "blunt" (the radii are both too large compared with an ideal hyperbolic QUISTOR), its field can be described as an quadrupole field, distorted by the superposition of an octopole field. This is one of the most likely field distortions for QUISTORs.

If in such a case, for a given ion mass m, the above sum resonance condition for octopoles is valid, the ion starts to resonate in the field and to take up energy from the RF field in both z and r directions. The oscillation amplitudes increase in both directions. Since the fourth order terms have the same sign in both directions, the frequencies of the oscillations in both directions either increase or decrease together. In both cases, the resonance condition is no longer fulfilled, and the resonance stops. This behaviour can easily be studied by simulations. - Other types of distortions by single multipoles show similar effects.

The quadrupole field can be also distorted by too blunt end cap electrodes, and a too sharp ring electrode (Q > 4.000), or vice versa (Q < 4.000). These cases have not yet been investigated. Most prominent additional terms of the electrical potential are pure and mixed terms of fourth order in r and z, as in the case of superimposed octopoles, but with different signs in r and in z directions. The resonance condition $\beta_z + \beta_r = 1$, remains valid in this case.

Up to a few years ago, the QUISTOR was operated mostly in the so-called "mass selective ion storage mode". After each ionization period, only a preselected single kind of ions was stored by applying corresponding operating conditions near the tip of the stability region, and subsequently measured by ejection through one of the end cap electrodes. A spectrum was acquired by frequent repetitions of this procedure with slightly altered storage conditions for the storage and subsequent detection of ions having different masses.

In the context of the present invention, this method is not regarded as a "scan" method. Hereafter, the term "scan method" is used to designate the measurement of the ions in a wide range of ion masses which are generated in a single ionization process, and stored simultaneously in the QUISTOR.

Up to now, the "mass selective instability ejection method" described in US-A-4,540,884 is the only ion

ejection scan method which has become known.

In its simplest form, this method operates the QUISTOR along the line a = 0 of the a_z/q_z-diagram shown in Fig. 2 only, i.e., the QUISTOR is driven in the "RF only" mode without applying a superimposed DC voltage. In this mode, theoretically all ions having a mass above a lower cut-off mass, can be stored within the QUISTOR. The cut-off ion mass is given by the limit of the stability area on the q axis :

$$m_{cut-off} = \frac{4 * e * V_{stor}}{q_{z,1} * r_0^2 * {}^2}, \text{ wherein}$$

$q_{z,1}$ = 0,91 limit of the stability area for a = 0, (characterized by $\beta_z = 1$)
e = charge of the electron
V_{stor} = peak amplitude of the basic RF voltage
r_0 = inner radius of the ring electrode
$\omega = 2 * \pi * f_{stor}$ angular frequency of the basic RF voltage

As can be seen from the above formula, $m_{cut-off}$ at the border of the stability area is direct proportional to the amplitude V_{stor} of the basic RF voltage. By scanning V_{stor} to higher values, the storage condition for one ion mass after the other shifts across the stability limit and the movement of the ions become unstable. It is of interest to note that only the ion movement in z direction becomes unstable ($\beta_z > 1$). The secular oscillations in r direction remain stable ($\beta_r = 0.34$). Thus, the ions do not longer encounter a backpulling central force in z direction. In contrast, in the z direction the averaged central force reverses its direction and the ions are driven against the end cap electrodes of the QUISTOR.

If the tip of one of the end cap electrodes is perforated, a fraction of the ions penetrates through the perforations and can be detected outside the QUISTOR by well-known mass spectrometric means, e.g. by a secondary electron multiplier.

This scan method, however, has two severe fundamental drawbacks:

First, only a small part of the ions hits the perforations in the center of the end cap electrode, whereas a major part of the ions hits the end cap electrode far off from the z axis. The secular frequency movement of the ions in r direction makes the probability very small that an ion resides - at a given time - near the z axis. - It is a difficult task to increase the perforated area and to focus the penetrating ions onto the detection device. Due to the high RF peak voltages V_{stor}, the ions partially have very high kinetic energies (up to 1000 eV and more) when they leave the QUISTOR, and a simultaneous focussing of all ions is thus impossible.

Second, ions situated close to the center of the field do not see very much of a field because the field in the center is exactly zero. Ions near the center do not leave the QUISTOR, unless they are hit by another particle, leave the center under the effect of the pulse transfer, encounter a destabilizing field outside the center, and move towards one of the end cap electrodes. In fact, not only the ions near the center are not ejected immediately, but all ions which move almost inside the r plane. At low pressure within the QUISTOR, this process of kicking the ions out of the r plane takes time. At a given scan speed, on the other hand, a long time to leave decreases the spectral resolution.

Both problems connected with these drawbacks can be at least partially overcome by the introduction of a damping gas. As shown in US-A-4,540,884, a damping gas (e.g. Helium) increases the spectrum resolution and the ion yield considerably. Both effects can be explained by above considerations. On one hand, the secular movements are damped, and the ions are concentrated near the center. On the other hand, frequent collisions of particles do not allow for long ion residing periods in the field-free center or in the r plane which is free of z field components.

According to our investigations, for a QUISTOR with radius r_0 = 1 cm and a storage frequency of 1 MHz, the optimum pressure for Helium as a dampiong gas is very near to 1,5 * 10^{-3} mbar, and the corresponding minimum leaving time for 95 % of the ions of one mass during a linear V_{stor} scan is about 200 μs.

The use of a damping gas, however, has not only positive results, but introduces severe drawbacks also, because it restricts the applicable ionization methods in the QUISTOR. Such a high pressure does not longer allow to choose freely an ionization method like electron bombardment (EI) or photon ionization (PI). Under the effect of the high damping gas pressure and the rather long storage times of ions within the QUISTOR, all primary ionization processes will be followed by charge exchange ionization ((CE) or chemical ionization (CI) processes which completely change the ionization characteristics and the appearance of the spectra.

Using Helium as a damping gas and electron bombardment as primary ionization, Helium charge

exchange (He-CE) ionization is the prevailing process. This may not be immediately recognized by an unexperienced user because the He-CE spectra resemble very much of low voltage EI spectra (the high 24.6 eV ionization energy of He serves partially for molecule fragmentation very similar to those of low energy electron collisions). The addition of small amounts of water or other CI reactant gases, however, exhibits immediately the onset of the corresponding CI reactions. This labile behaviour of the QUISTOR in the presence of He damping gas makes it hard to use for reliable analysis purposes.

Therefore, it is the object of the present invention to improve the scan technique and to eliminate the severe drawbacks of the presently known scanning methods by ion ejection.

This object is met by the invention as defined in the characterizing part of claim 1. As may be gathered therefrom, the present invention deals with a new scanning method which may be called "mass selective resonance ejection" of ions and makes use of the resonance of the secular movements in an exciting field.

In contrast to the "mass selective instability ejection", this "mass selective resonance ejection" takes place inside the ion stability region, usually even from such spots inside the stability area where the ion storage stability is especially large. (The storage stability may be defined as resistance against defocussing DC fields. The stability diagram of Fig. 2 reveals that at $q_z = 0.78$ the point of maximum stability can be found because here positive or negative DC voltages of maximum strength can be applied without destroying the storage capability for the respective ions). During the mass selective resonance ejection, the ion movements never become instable but the amplitude of the movement is increased steadily by the resonance effect.

The scan method by "mass selective resonance ejection" needs additional electrical circuitry: An excitation RF voltage with frequency f_{exc} has to be applied across the end cap electrodes of the QUISTOR.

In the mass selective resonance ejection scan, the excitation voltage frequency f_{exc} must match the z direction secular frequency $f_{sec,z}$ of the ions to be ejected. The ions then take up energy from the excitation field, their movement amplitude in z direction increases, and they finally hit the end cap electrodes. If these are perforated, a fraction of the ions penetrates and can be detected outside the QUISTOR as described above for the case of mass selective instability ejection.

This "mass selective resonance ejection" eliminates one of the two fundamental drawbacks of the "mass selective instability method": Ions near the center of the field and within the r plane see the full excitation voltage and start immediately to oscillate in z direction. The ejection, therefore, is much faster in the resonance ejection mode. The average leaving time is about 120 µs; the scan speed, therefore, can be made considerably faster than for the mass selective instability ejection. The line shape of the mass selective resonance ejection is by far better than that of the mass selective instability ejection, since the tailing of the slowly leaving ions from the center lacks completely.

There are several possibilities to scan over subsequent ion masses. The two simplest methods are, first, to scan the excitation frequency f_{exc} at fixed RF voltage amplitude V_{stor}, and, second, to scan the RF voltage amplitude V_{stor} at fixed excitation frequency f_{exc}.

The excitation frequency scan provides for a variation of the excitation frequency f_{exc} either upwards from 0 to $f_{stor}/2$ or downwards from $f_{stor}/2$ to 0. The upwards scan excites ions having masses down from infinity to $m_{cut-off}$, whereas the downwards scan ejects the masses upwards.

In both scan directions, the excitation frequency scan exhibits some minor drawbacks. First, the scan exhibits excellent results only in small mass ranges because there exist several natural resonances of the secular frequencies along the scan, depending on field distortions. Second, the masses are not linearly dependent on the frequency. It is not even possible to calculate the mass scale in a simple way since the relationship between q_z (proportional to 1/m) and β_z (proportional to f_{exc}) cannot be expressed by an explicit analytical expression. Of course, the computability of the mass scale plays a minor role only because in practice the mass scale is calibrated experimentally. It is, however, useful to start the calibration from a theoretical curve.

These two minor drawbacks make this type of scan less favourable than the scan of the RF voltage V_{stor}.

The RF voltage amplitude scan with fixed excitation frequency f_{exc} can only be performed in one direction: Since the instability boarder of the stability diagram follows the resonance ejection in a fixed mass relationship, the scan cannot - for obvious reasons - be carried out in the other direction.

This type of scan has some advantages over the excitation frequency scan: The mass-scan is theoretically linear with the scan parameter V_{stor}, and the scan works equally good over the whole range of stored masses.

The second fundamental drawback of the mass specific instability ejection, the low yield of ions through the small perforated area of the end cap electrodes is not yet eliminated.

Both types of scan, however, can be still improved considerably if the QUISTOR has field faults which

result in non-harmonic oscillations. Scan speed and scan direction then show a marked influence onto the quality and resolution of spectrum peaks. Thus, the invention also comprises the QUISTOR as defined by the characterizing part of claim 10.

In such a QUISTOR the frequency of the secular oscillations changes with the amplitude of the oscillations. If an ion increases its secular frequency with amplitude (positive terms of fourth order), it will only stay in resonance with the exciting voltage for a longer period of time, if the frequency of the exciting field increases at the same speed during the scan. If the correct scan speed is applied, there is a typical double resonance effect: the secular frequency is in resonance with the exciting frequency, and the increasing rate of the secular frequency is in resonance with the scan speed.

Using a QUISTOR with such field distortions, the upward scan of the frequency gives experimentally by far better results than the downward scan. Spectrum resolution and ion yield are significantly better. A resolution in excess of $R = 1200$ has been achieved over small mass ranges, as shown in fig. 7. The downwards scan with the same QUISTOR did not show a resolution better than 1/10 of the above value.

Naturally, this type of resonance is not as sharp as the resonance of the secular frequency with the excitation frequency because the scan speed has to hold the ion within resonance for a short period of time only. The resonance maximum is very wide, and deviations by a factor of two do not seriously destroy, the effect. This type of scan may be called "mass selective double-resonance scan".

A further enhancement of the RF voltage scan, however, is possible by making use of specific natural resonances in a non-ideal QUISTOR. This type of scan may be designated as "mass selective triple-resonance ejection".

As described above, field faults of fourth order produce a coupling resonance effect between the secular oscillations in r and z direction at the location $\beta_z + \beta_r = 1$. If the distortions are produced by a QUISTOR obeying one of the conditions for the distance-corrected ratio Q of the inscribed pole radii

$Q < 4.000$ or $Q > 4.000$,

resonating ions see an increase of their secular movement amplitude in z direction, and a decrease in r direction. Thus, the ions are focussed in z direction during z ejection, and are ideally suited for a high-gain ejection through a small perforated area at the tip of one of the end cap electrodes.

It is now possible to apply the mass selective resonance ejection with fixed excitation frequency and RF voltage amplitude scan to such a QUISTOR with such field distortions of fourth order, to tune the excitation frequency exactly into such a natural coupling resonance, and to adjust the scan speed to keep the ions in resonance.

Three resonance phenomena appear simultaneously:

First, the resonating ions take up energy from the excitation field and increase their oscillation amplitudes in z direction.

Second, the ion movement in z direction gains additional energy from the coupled movement in r direction. The ions are gathered near the z axis. The secular frequency of the ions becomes slower in z direction, and higher in r direction, and the condition $\beta_r + \beta_z = 1$ remains nearly fulfilled by a partial compensation. The compensation, however, is only nearly exact, if the amplitudes are similarly large. If the r amplitude is small the r secular frequency changes only very slowly, and the compensation stops. - This resonance concentrates the ions near the z axis and increases largely the ion gain.

Third, the V_{stor} upwards scan increases the secular frequencies of a given ion. This compensates the decreasing secular frequency in z direction which stems from the increasing amplitude. If the scan speed is correctly chosen, the ions are held in resonance with the exciting frequency.

In a well-tuned system, the ions leave the QUISTOR very near to the z axis. Almost all the ions penetrate the perforations at the tip of the end cap electrode. To direct the ions to the correct end cap electrode, a field fault of third order might be introduced, or a small DC voltage may be applied between both end cap electrodes, in addition to the exciting frequency. The ion yield supercedes that of the damping gas optimized mass selective instability ejection scan by a factor of more than ten, i.e., this type of triple resonance scan makes a tenfold better use of the ions stored in a QUISTOR.

The time to leave the QUISTOR is extremely short in the case of the triple resonance: it was possible to produce, with a QUISTOR of selected design, completely resolved spectra at scan speeds of one mass unit in 36 μs only, i.e., all ions of a given mass-to-charge ratio were ejected in 36 periods of the basic RF voltage only, or in only 12 oscillations of the secular frequency. This is about six times faster than the maximum speed for the "mass selective instability ejection scan", each scan exhibiting tenfold the gain.

There is another big advantage of this triple-resonance scan: it does not necessarily need any collision or damping gas, but works in the usual mass spectrometric vacuum pressure range from the best vacua up to $6 \cdot 10^{-5}$ mbar, with a resolution optimum betwen 2 and $4 \cdot 10^{-5}$ mbar. Above this limit, the spectral lines tend to broaden, as is known from normal quadrupole mass spectrometers. This means that any type of

ionization can be used.

Besides normal vacua, higher yield, faster scan rates, and better line shape, the triple-resonance ejection scan possesses still another advantage over the mass selective instability ejection scan: It needs lower RF voltage amplitudes V for the ejection of the same masses. The mass instability limit is characterized by $q_{z,1}$ = 0.91, whereas the triple-resonance value is $q_{z,reson}$ = 0.82. Since the q values are reversely proportional to the masses, the triple-resonance scan needs a voltage lower by about 9 % for the same mass. This is a considerable advantage because the generation of the high-voltage RF is one of the most difficult tasks in the design of QUISTORs.

In practice, the triple-resonance scan sometimes exhibits a very bad peak shape which is caused by a beat between the exciting high frequency voltage, and a small fraction (in most cases 1/3 or 1/4) of the high frequency storing voltage. In this case, the electrodes of the QUISTOR can be formed with such a distance-corrected ratio Q of the radii that one of the natural resonance frequencies of the secular ion movement coincides exactly with the fraction of the high frequency storage voltage. If the exciting high frequency voltage then is generated from the storage high frèquency (e.g. by frequency division), the peak shape of the ions in the spectrum is excellent.

One way of carrying out the invention is described in detail below with reference to drawings which illustrate only one specific embodiment of a QUISTOR and the results of measurement performed therewith. In the drawings,

Fig. 3 is a schematic crossectional view of a QUISTOR designed and used for performing the method according to the invention and

Fig. 4 is a spectrum obtained in the QUISTOR shown in Fig. 3 by means of an RF voltage amplitude scan after CI ionization, from a mixture containing tetrachloroethene, toluene and acetone,

Fig. 5 is the molecular ion group of tetrachloroethene -enlarged from the spectrum of Fig. 4,

Fig. 6 is a single shot enlargement from an extrmeley fast scan, comprising the molecular group of tetrachloroethene similar to Fig. 5 but obtained after EI ioniziation, and

Fig. 7 is a portion of a spectrum illustrating the mass resolution in case of an excitation frequency upwards scan.

The QUISTOR mass spectrometer shown in Fig. 3 includes a hyperbolically formed ring electrode 11 and end cap electrodes 12, 13 with an angle 1:1.3784 of the hyperbole asymptotes, giving a Q = 3.610. The electrodes are correctly spaced by insulators 14, 15. The natural resonance frequency $f_{res,z}$ obeying the condition

$f_{res,z} + f_{rez,r} = f_{stor}/2$,

matches exactly 1/3 of the storage high frequency f_{stor}.

To the ring electrode 11 a storage RF-generator 16 is connected. Similarly, to one of the cap electrodes 13 an exciting RF-generator 17 is connected. Using a storage frequency of f_{stor} = 1 MHz, the exciting frequency is f_{exc} = 333.333 kHz. The latter can be advantageously generated by dividing the frequency of the storage RF-generator 16, so that the exciting RF-generator 17 may be formed by a frequency divider connected to the storage RF-generator 16 as indicated by broken line 18. The optimum voltage of the exciting frequency depends on the scan speed, and ranges from 1 V to about 20 V.

With an inner radius of the ring electrode 11 of r_r = 1 cm, and with ions stored in the QUISTOR during a preceding ionization phase, a scan of the high frequency storing voltage V_{stor} from a minimum value upwards to 7.5 kV yields a spectrum up to more than 500 atomic mass units in a single scan.

Ions may be formed by an electron beam which is generated by a heated filament 21 and a lens plate 22 which focusses the electrons through a hole 23 in the end cap electrode 12 into the QUISTOR during the ionization phase, and stops the electron beam during other time phases. During the scan period, ions are ejected through the perforations 24 in the end cap electrode 13 and measured by a multiplier 25.

With this QUISTOR, a CI spectrum of acetone, toluene, and tetrachloroethene was measured. The full spectrum covered the mass range from 39 u to 500 u, the section from 39 u to nearly 180 u being shown in Fig. 4. The spectrum was taken by means of an RF voltage amplitude scan. Fig. 4 is the spectrum of a single shot taken in 33 ms. A spectra repetition rate of 25 spectra/s left time for 250 µs of quenching, 1 ms of ionisation and 5 ms of CI reaction. Fig. 4 illustrates the high resolution and the high sensitivity which is achieved with this method even in a single shot. This fact is emphasized by the enlarged section from Fig. 4 shown in Fig. 5, which section comprises the molecular group of tetrachloroethene. As a second example, Fig. 6 shows the tetrachloroethene comprising enlargement of a single shot spectrum similar to Fig 4, but taken in 8 ms from mass 30 u to mass 180 u with a repetition rate of 100 spectra/s and making use of EI ionisation.

As a comparison, Fig. 7 finally shows the mass resolution achieved in a spectrum produced by means of an upwards scan of the excitation frequency. Here again, Fig. 7 shows a single shot. The resolution achieved was r = 1200.

Claims

1. The method of mass analyzing a sample which comprises the steps of
a) defining an electrical field condition comprising a three-dimensional electrical quadrupole storage field including an RF component, which quadrupole storage field is appropriate to simultaneously trap sample ions over an entire mass range of interest,
b) introducing sample ions into or creating sample ions within the quadrupole storage field whereby ions within the mass range of interest are simultaneously trapped and perform ion-mass specific secular movements,
c) changing the electrical field condition so that simultaneously and stably trapped ions of consecutive masses leave the storage field,
d) detecting the ions of sequential masses as they leave the storage field, and
e) providing an output signal indicative of the ion masses,
characterized in that
f) as a component of the electrical field condition, an exciting RF field is generated, the frequency of said exciting RF field being different from the frequency of the RF component of said quadrupole storage field, and that
g) the electrical field condition is changed in step c) in such a way that ions of consecutive masses encounter a resonance of their secular movements with the exciting RF field, so that they take up energy, increase thereby their secular movement, and finally leave the trapping field.

2. The method of claim 1 in which the electrical field condition is generated by a QUISTOR of the type having a ring electrode and spaced end cap electrodes, wherein the storage field is defined by U, V_{stor} and f_{stor}, and the exciting field is defined by V_{exc} and f_{exc}, and in which the field condition is changed by modifying one or more of U, V_{stor}, f_{stor}, or f_{exc}, where
U = amplitude of storage DC voltage between the ring electrode and the end electrodes
V_{stor} = magnitude of storage RF voltage between ring electrode and end electrodes
f_{stor} = frequency of storage RF voltage
V_{exc} = magnitude of exciting RF voltage between the two end electrodes
f_{exc} = frequency of exciting RF voltage.

3. The method of claim 2 in which f_{exc} is set constant, and essentially only V_{stor} is changed.

4. The method of claim 3 in which the constant frequency f_{exc} of the exciting RF voltage matches a natural sum or coupling resonance frequency of the secular ion movements arising from geometrical deviations of the storing field from the ideal hyperbolic shape with angle 1:1.414 of the asymptotes, or electrical deviations of the RF voltage from ideal sine waves.

5. The method of claim 4 in which said natural sum or coupling resonances of the secular movements of the ions are generated by geometrical deviations of the storing field introduced by deviations of the shape of the ring and end electrodes from the ideal hyperbolic form with angle 1:1.414 of the asymptotes.

6. The method of claim 5 in which the radii of the curved end electrodes and of the curved ring electrode, both defined in the points nearest to the field center, in order to generate the natural resonances of the secular movements obey the condition
$0.500 < Q < 3.990$
or $4.010 < Q < 25.0$, where

$$Q = \frac{R_e}{R_r} * \frac{r_0}{z_0},$$

R_e = radius of the end electrodes in the points nearest to the field center
R_r = radius of the ring electrode in the points nearest to the field center
r_0 = smallest distance of the ring electrode from the field center
Z_0 = smallest distance of the end electrodes from the field center.

7. The method as in one of the claims 4 to 6 in which the shape of the QUISTOR electrodes are chosen so that the natural coupling resonance frequency of the secular ion movements coincides with a low fraction 1/n (n = small integer number greater than 2) of the storage frequency, and in which the excitation voltage with frequency $f_{exc} = f_{stor}/n$ is coupled in frequency and phase to the storage voltage with frequency f_{stor}.

8. The method as in claim 7 in which n = 3.

9. The method as in one of the claims 1 through 8 in which the scanning speed for the parameters of the superimposed fields is chosen such that the shift of the secular frequency with increasing amplitude, caused by an anharmonic storage field, is at least partially compensated by an inverse shift of the secular frequency caused by the parameter scanning itself.

10. A QUISTOR specially designed for performing the method according to any one of claims 1 to 9, comprising a toroidal ring electrode (11), first and second end cap electrodes (12, 13) mounted in coaxial relationship to and axially spaced from said ring electrode (11), said first end cap electrode (12) having a central hole (23) therein and said second end electrode (17) having central perforations (24), a storage RF-generator (16) connected to said ring electrode (11), ionisation means (21, 22) mounted outside the first end cap electrode (12) in register with said hole (23), and ion detection means (25) mounted outside said second cap electrode (13) in register with said perforations (24),
characterized in that
to the said second end cap electrode (13) an exciting RF-generator (17) is connected and that the shapes of said ring and said end cap electrodes (11, 12, 13) deviate from the ideal hyperbolic shape having an angle 1:1.414 of the asymptotes in order to provide field faults resulting in non-harmonic oscillations of the ions trapped within the QUISTOR.

11. The QUISTOR of claim 10, characterized in that at least one of the RF-generators (16, 17) is arranged to produce RF-signals being different from ideal sine waves.

12. The QUISTOR of claim 10 or 11, characterized in that the radii of the end cap electrodes (12, 13) and of the toroidal ring electrode (11), both defined in the points nearest to the field center, in order to generate the resonances of the secular movements obey the condition
$0.500 < Q < 3.990$
or $4.010 < Q < 25.0$, where

$$Q = \frac{R_e}{R_r} * \frac{r_0}{z_0},$$

R_e = radius of the end cap electrodes (12, 13) in the points nearest to the field center
R_r = radius of the ring electrode (11) in the points nearest to the field center
r_0 = smallest distance of the ring electrode (11) from the field center
z_0 = smallest distance of the end cap electrodes (12, 13) from the field center.

13. The QUISTOR as in one of the claims 10 to 12, characterized in that the shape of the QUISTOR electrodes (11, 12, 13) are chosen so that the coupling resonance frequency of the secular ion movements coincides with a low fraction 1/n (n = small integer number greater than 2) of the storage frequency produced by storage RF-generator (16), and in that the excitation RF-generator (17) produces an excitation voltage having the frequency $f_{exc} = f_{stor}/n$, the excitation RF-generator (17) being coupled in frequency and phase to the storage RF-generator (16).

14. The QUISTOR as in claim 13, characterized in that n = 3.

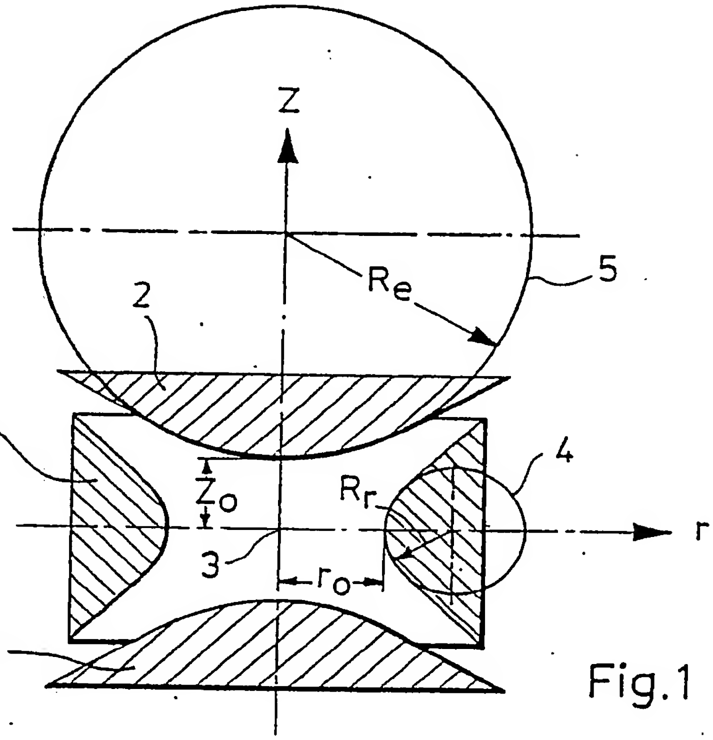

Z
Re
5
2
1
4
Zo
Rr
r
3
ro
2

Fig.1

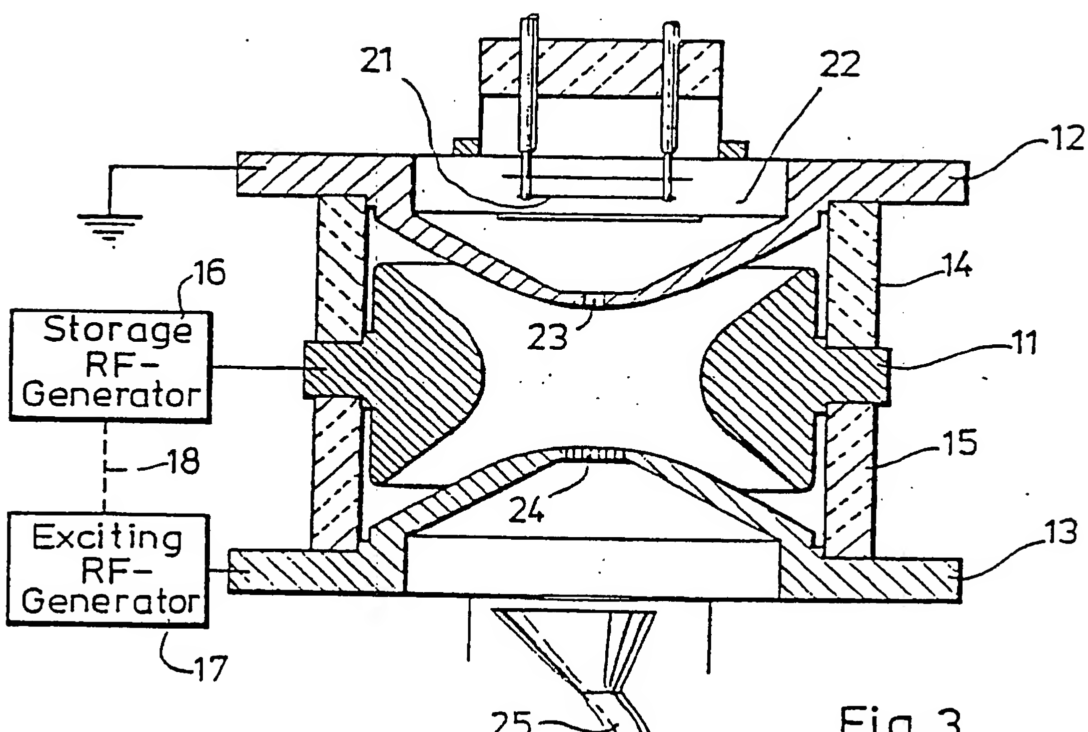
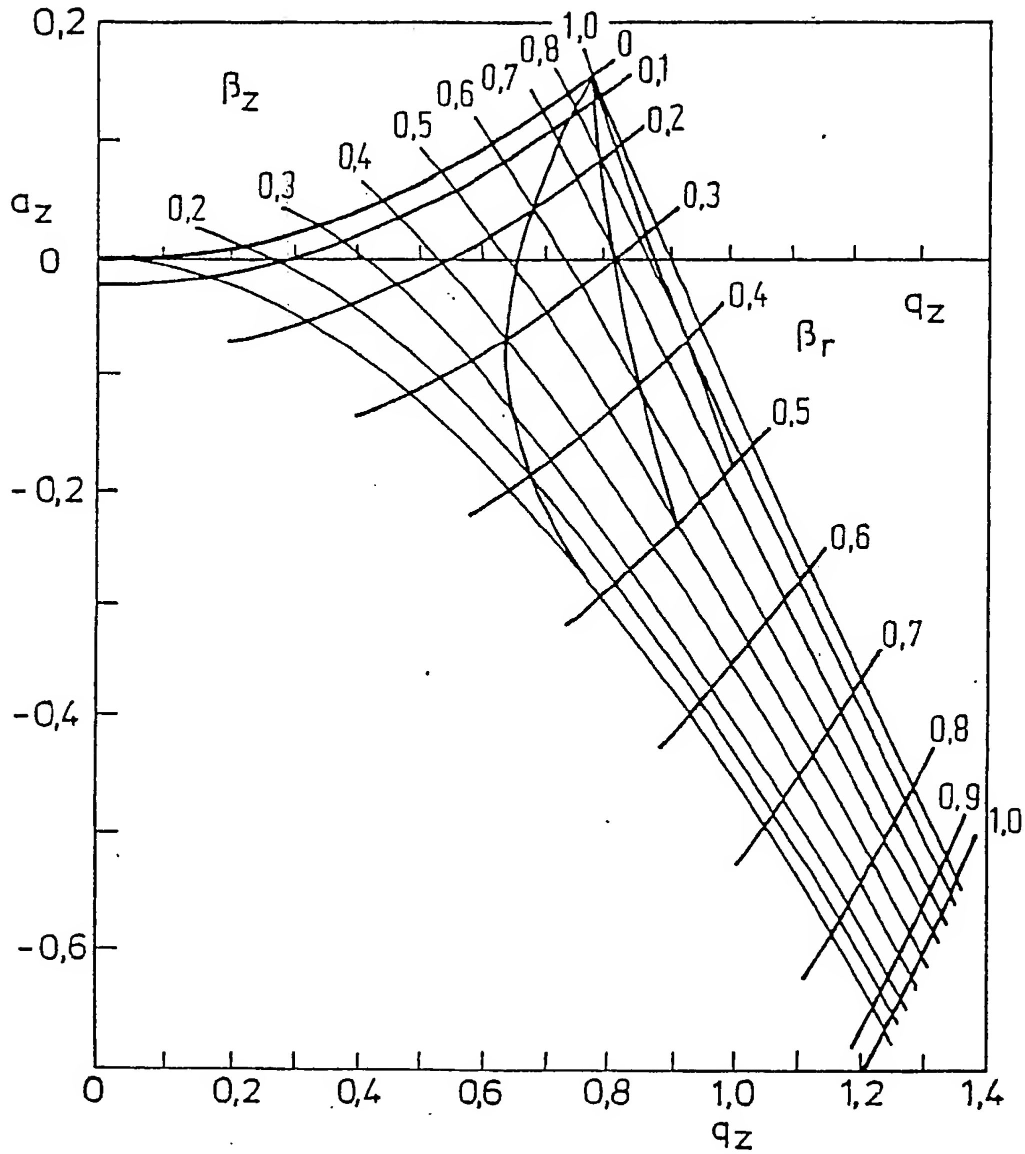

21
22
12
16
14
Storage RF-Generator
23
11
18
15
Exciting RF-Generator
24
13
17
25

Fig.3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-0,2
-0,4
-0,6
a_z
0
β_z
β_r
q_z
1,0
0,8
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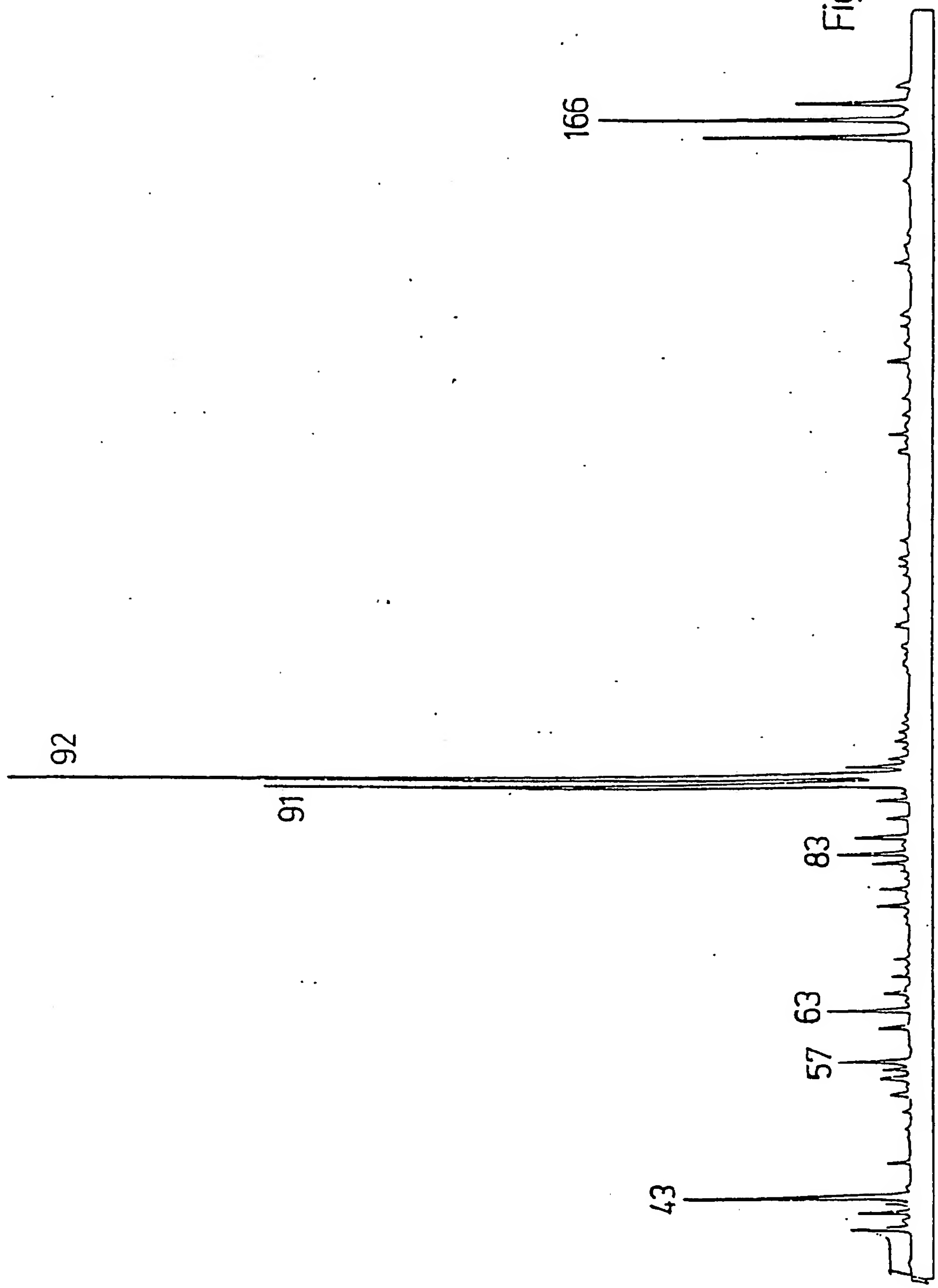
0,6
0,5
0,4
0,3
0,2
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0
0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
q_z

Fig. 2

Fig.4



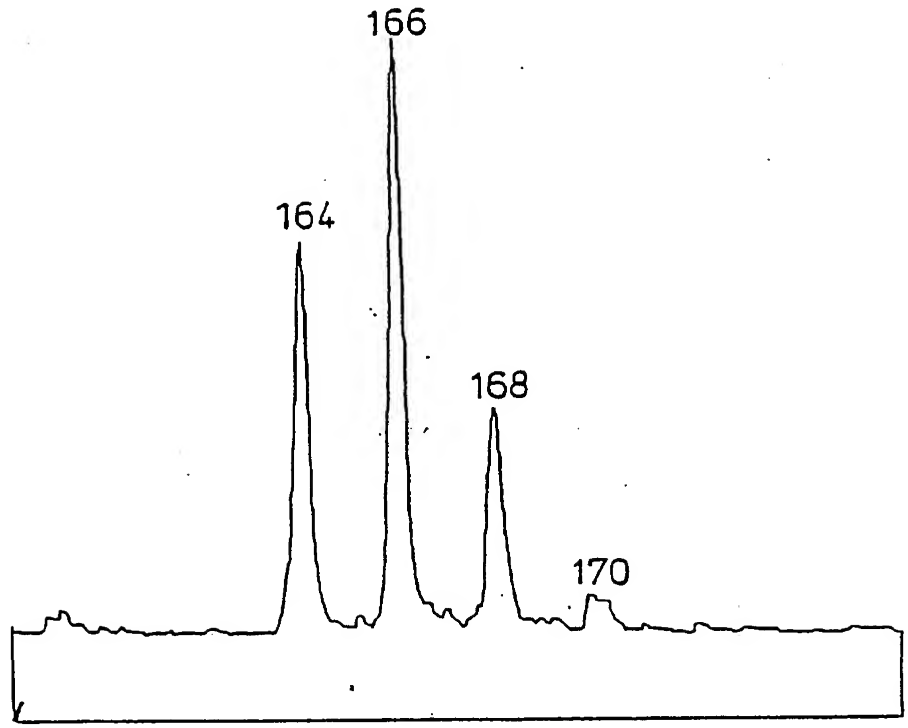


Fig.5

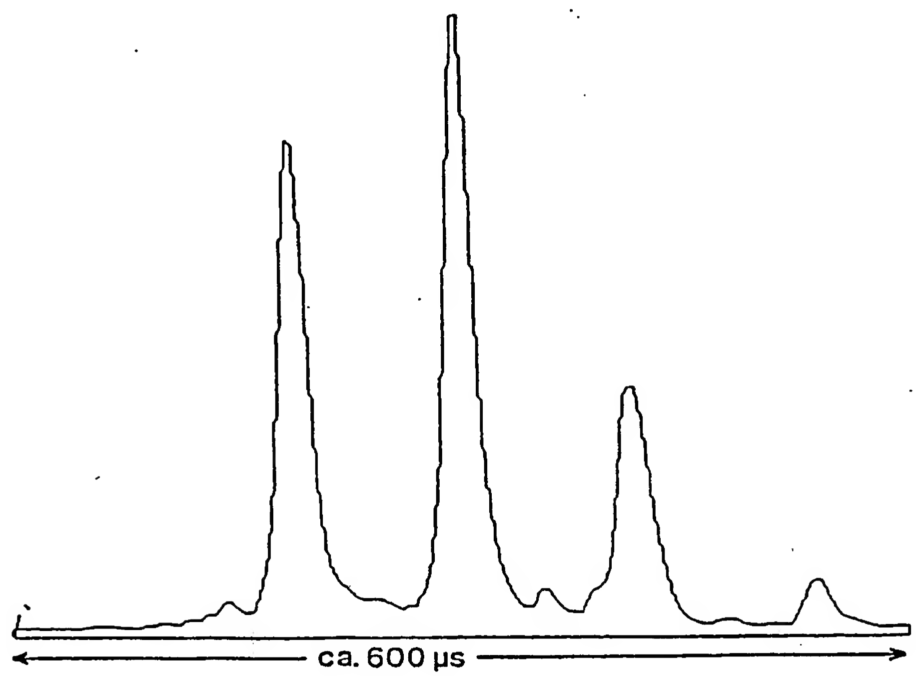


Fig.6

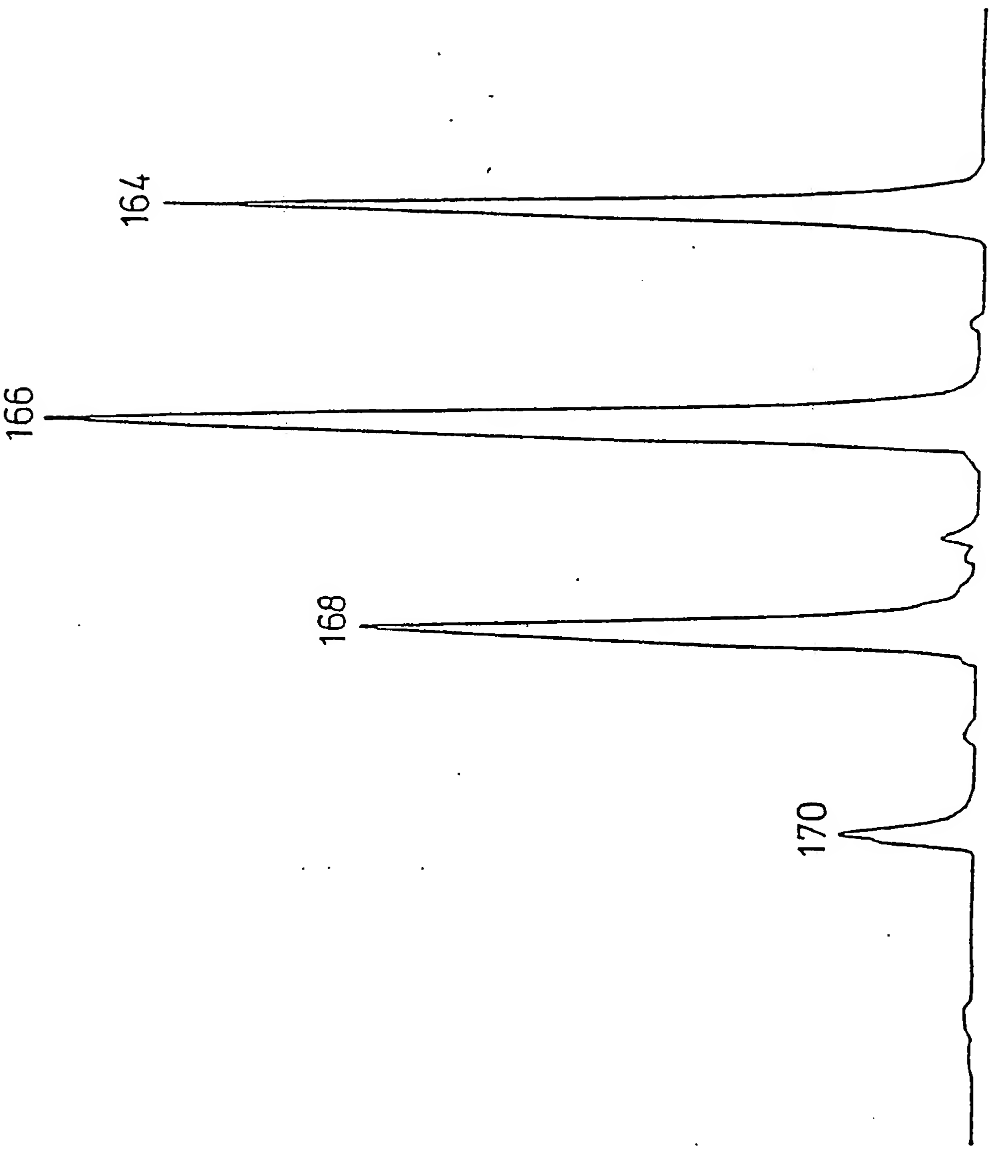


Fig. 7

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 10 5847

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 202 943 (FINNIGAN CORP.) * Page 2, lines 3-10; page 3, line 33 - page 4, line 13; page 8, lines 10-25; page 9, lines 6-8; page 10, lines 3-13; page 11, lines 1-7; page 12, lines 16-27; figures 1,2 * ---	1-3,5,6,10-12	H 01 J 49/42
A,D	US-A-2 939 952 (W. PAUL et al.) * Column 5, lines 70-75; figures 11,12 * -----	1-14	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			H 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02-12-1988	WINKELMAN,A.M.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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